

Materials with Colossal Dielectric Constant: Do They Exist?

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Experimental evidence is provided that colossal dielectric constants $\epsilon' \geq 1000$, sometimes reported to exist in a broad temperature range, can often be explained by Maxwell-Wagner type contributions of depletion layers at the interface between sample and contacts, or at grain boundaries. We demonstrate this on a variety of different materials. We speculate that the largest intrinsic dielectric constant observed so far in non-ferroelectric materials is of order 10^2 .

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Materials exhibiting a colossal dielectric constant (CDC), $\epsilon' > 10^3$, have recently gained considerable attention. CDC behavior is of technical importance for applications using high- ϵ electronic materials, such as random access memories based on capacitive elements. Fundamental interest was initiated by the observation of CDC behavior in some high- T_c parent compounds [1,2]. Indeed, CDC behavior may indicate a colossal polarizability, which was invoked in early polaronic and bipolaronic models as a possible mechanism for high- T_c superconductivity [3]. During the last decade, similar observations of CDC behavior have been reported in an increasing number of materials, such as transition metal oxides [4–6].

Large dielectric constants are expected for ferroelectrics in a narrow temperature range close to T_c , or for systems with hopping charge carriers yielding a dielectric constant that diverges towards low frequencies. However, in various recent reports [1,2,4–6] giant values of the dielectric constant were claimed to persist over broad temperature ranges and, when plotted as a function of frequency, revealing an almost constant low-frequency value and a step-like decrease of the dielectric constant towards higher frequencies. This step-like decrease, which is accompanied by a loss peak in the imaginary part of the permittivity, ϵ'' , shifts exponentially to higher frequencies with increasing temperature, characteristic of Debye-like dipolar relaxation with a thermally activated relaxation rate. Several intrinsic physical interpretations have been given. Examples include almost incipient ferroelectricity in high- T_c materials [2], highly polarizable relaxation modes [5], or a relaxor-like slowing down of dipolar fluctuations in nano-size domains [6].

In the present letter we provide evidence that many of these observations are not intrinsic in origin and we speculate that most, if not all, of the CDCs reported so far are based on Maxwell-Wagner type extrinsic effects [7]. We will promote the notion that the most natural explanation of apparent CDCs are contact effects, and that in ceramic samples grain boundary effects may play a similar role and further "enhance" the dielectric

constant. At these interfaces (metal to insulator contacts, inter-grain boundaries) depletion layers are formed yielding Maxwell-Wagner type relaxations when measured by standard dielectric techniques that use metallic electrodes and two point contact configurations. Thus, while some of the reports may indeed be based on intrinsic effects, extrinsic effects have to be excluded by carefully studying the materials using different sample geometries, different contact configurations, and analyzing the results in terms of electronic networks as considered in detail decades ago [8,9]. In the present letter, we propose a simple network that is derived from the models outlined by the classical works of Jonscher [8], Macdonald [9], and others, and also from our years of experience in dielectric spectroscopy on doped semiconductors. We show examples on a series of different materials, where we observed CDCs, all of which being due to contact effects. Most of the investigated samples are single crystals, but we also provide results on a ceramic sample to evidence effects of grain boundaries on the dielectric response. Finally, in addition to the analysis in terms of electronic networks, we will make some suggestions on experiments that exclude extrinsic effects.

The inset to Fig. 1a shows the equivalent circuit that describes the main features of the dielectric response of almost all doped or dirty semiconductors. The circuit consists of a leaky capacitor connected in series with the bulk sample. As indicated in the equivalent circuit, the intrinsic bulk response is given by the sum of dc conductivity (σ_{dc}), frequency-dependent ac conductivity - for which we use the universal dielectric response (UDR) ansatz $\sigma'_{ac} = \sigma_0 \omega^s$, $s < 1$ [8,10] - and the high-frequency dielectric constant ϵ_∞ [11]. The UDR is the most common approach to take into account hopping conductivity of localized charge carriers [12]. Under these assumptions, the intrinsic complex conductivity $\sigma_{intrinsic}^* = \sigma'_i + i\sigma''_i$ is given by [8,10]

$$\sigma'_i = \sigma_{dc} + \sigma_0 \omega^s, \quad (1)$$

$$\sigma''_i = \tan\left(\frac{s\pi}{2}\right) \sigma_0 \omega^s + \omega \epsilon_0 \epsilon_\infty, \quad (2)$$

where ε_0 is the permittivity of free space. From the conductivity, the complex dielectric permittivity can be calculated by $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) = i\sigma^*(\omega)/\omega\varepsilon_0$. This formalism does not assume any dipolar relaxation phenomenon in the compound under investigation. The leaky capacitor in the equivalent circuit of Fig. 1a represents the most common way to model contributions from the electrode-sample interface [8,9]. For semiconducting samples, these arise mainly due to the formation of Schottky barriers in the region close to the metallic electrodes. If the electron work function in a metal is higher than in an electron semiconductor, then in the contact region of the semiconductor the electron concentration is suppressed, and a depletion layer appears. This relatively thin layer of small conductivity, acts as a high capacitance in parallel with a large resistor, connected in series to the bulk sample. But also an accumulation of defects or deviations from stoichiometry (e.g. oxygen deficiency) near the sample surface may lead to such a capacitive surface layer.

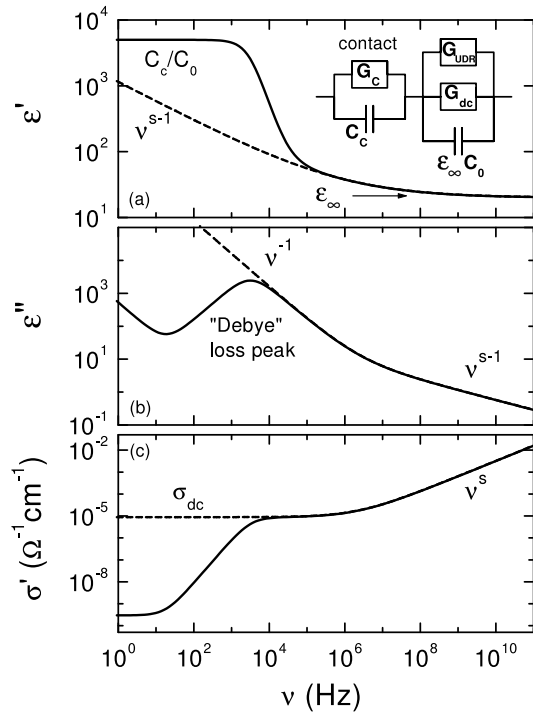


FIG. 1. Frequency-dependent dielectric response for the equivalent circuit shown in Fig. 1a. Solid lines: overall response, dashed lines: intrinsic bulk response as given by eqs. (1) and (2). The circuit parameters have been chosen to reveal the prototypical behavior of doped semiconductors with Schottky-barrier type contacts.

The prototypical dielectric response that results from the equivalent circuit of Fig. 1a is shown in Fig. 1. The solid lines represent the full dielectric response, the response of the intrinsic part alone is indicated by the dashed lines. At low frequencies, $\sigma'(\omega)$ (Fig. 1c) exhibits a step-like increase, which can be ascribed to a

successive bridging of the contact resistance (dominating the low-frequency response) by the contact capacitance acting like a short at high frequencies. The intrinsic contribution, following Eq. (1), is revealed only at high frequencies. Via the relation $\varepsilon'' \sim \sigma'/\omega$, the step in $\sigma'(\omega)$ transfers into a peak in $\varepsilon''(\omega)$ (Fig. 1b), thereby resembling the response of a Debye-like dipolar relaxation process. It is accompanied by a large step-like increase of $\varepsilon'(\omega)$ towards low frequencies (Fig. 1a). At low frequencies $\varepsilon'(\omega)$ is dominated by the very high contact capacitance, C_c , which when divided by the empty capacitance of the sample C_0 , leads to the apparently colossal values of $\varepsilon' = C_c/C_0 > 10^3$. Also for $\varepsilon'(\omega)$, the intrinsic response is detected only at sufficiently high frequencies. The time constant of the circuit is approximately $\tau \sim RC_c$, with R being the intrinsic sample resistance. Assuming that the contact capacitance is nearly constant, the temperature dependence of the time constant is driven by the exponential increase of the charge carrier density of the semiconducting sample, leading to $\tau \sim R_0 C_c \exp(E/T)$, with E being a characteristic activation energy for charge carriers. Of course the contact step depends on the thickness and the capacitance of the depletion layer, and is strongly sample dependent in addition to its temperature dependence. We will show that in some cases at room temperature the contact step can be shifted well into the GHz frequency region. Before demonstrating this type of response in a series of samples, we would like to state that in some cases the electronic equivalent circuit, shown in the inset to Fig. 1a, is still too simple [11]. We have found that in more metallic samples the influence of inductance has to be taken into account at high frequencies, and sometimes the contacts are better represented using a distribution of time constants (several RC values). Furthermore, in ceramic samples other depletion layers can be formed at the interfaces of grain boundaries, yielding an additional step in $\varepsilon'(\omega)$ and further increase of the low-frequency dielectric constant. This will be demonstrated in one specific sample. However, we provide clear evidence that in most cases the simple equivalent circuit of Fig. 1a works rather well and accounts for the CDCs as well as for the relaxational behavior observed in many semiconducting dielectrics.

Our first example deals with measurements on single crystals of CdF_2 doped with indium with contacts made from sputtered gold (for details, see [13,14]). The experimental results and fits performed simultaneously for real and imaginary part with the simple equivalent circuit of Fig. 1a are shown in Fig. 2. Here $\varepsilon'(\omega)$ (Fig. 2a) and $\varepsilon''(\omega)$ (Fig. 2b) are shown in double-logarithmic representation. $\varepsilon'(\omega)$ exhibits the characteristic relaxation steps reaching low-frequency values of about 2000, which are accompanied by well pronounced loss peaks in $\varepsilon''(\omega)$. For the higher temperatures, at frequencies below the loss peaks, $\varepsilon''(\omega)$ shows a minimum marking the transition to the contact-dominated region. Compared to Fig. 1b, this minimum is rather shallow, but using

a distribution of contact barriers a very good agreement of fits and experimental data could be achieved. For the frequency and temperature range of Fig. 2, the UDR contribution can be neglected. In this specific semiconductor we carefully checked the influence of the contacts by measuring samples of different thickness and employing different contact electrodes. As an example, in Fig. 2 a second result obtained on the same sample ($T = 126$ K), but with the electrodes separated from the bulk by a thin insulating layer of mica [13,14], is given. Here no Schottky barriers are formed and the electrode capacitance is simply given by the mica layer. As shown by the dashed lines, the results can be fitted by the same equivalent circuit, leading to nearly identical bulk-, but markedly different contact-parameters. In both cases the intrinsic dielectric constant $\varepsilon_\infty \approx 10$ is far from being colossal or even unusually large. In order to exclude a Debye dipolar relaxation process, we also illuminated the sample by laser light [14]. It is obvious, that the Debye relaxation time τ_D should not depend on the light intensity. In our experiment the "relaxation frequency" $\omega_p = 1/\tau = 1/(RC_c)$ was proportional to the light intensity due to an increase of the charge carrier density of the semiconducting sample.

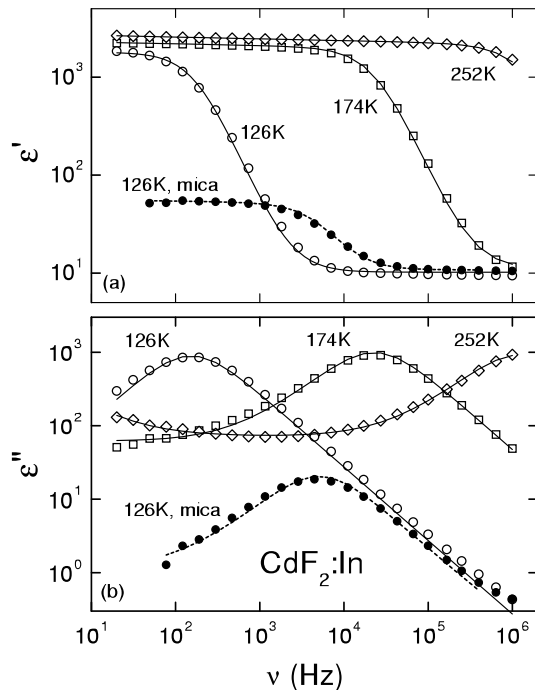


FIG. 2. Frequency-dependent dielectric response of single-crystalline CdF_2 with sputtered gold contacts for three temperatures (open symbols) [14]. The closed circles show the results at 126 K for the same sample with a thin layer of mica between sample and electrodes. The lines are fits with the equivalent circuit shown in Fig. 1a including a distribution of contact parameters.

Figure 3 shows $\varepsilon'(\omega)$ for three transition metal oxides, all exhibiting apparently colossal dielectric constants at

low frequencies. In Fig. 3a, the dielectric response of LaMnO_3 [15], the parent compound of all colossal magnetoresistance materials is given. Pure LaMnO_3 is an antiferromagnetic insulator. The finite carrier density probably results from a slight oxygen excess. The curves in Fig. 3a were taken at temperatures below the antiferromagnetic phase transition. Again we find the step-like decrease of ε' on increasing frequencies. The solid lines represent fits using our simple equivalent circuit. Here, the UDR had to be included in the fits, leading to a ω^{-1} contribution, which smears out the contact-dominated step in $\varepsilon'(\omega)$ at high frequencies. For the intrinsic dielectric constant we obtain, $\varepsilon_\infty \approx 15$. For doped manganates similar results were obtained, yielding somewhat higher, but certainly not colossal intrinsic dielectric constants [15,16]. We also want to refer the reader to our earlier work on single-crystalline $\text{La}_2\text{CuO}_{4+\delta}$, a parent compound of high- T_c materials, which also reveals high non-intrinsic values of ε' [17].

Figure 3b shows the results for single-crystalline $\text{SrNbO}_{3.41}$, which is derived from the high- T_c ferroelectric compound $\text{SrNbO}_{3.5}$, and has been characterized as one-dimensional metal [18]. In this case the intrinsic dielectric constant is rather high, reaching values of approximately 100. The low-frequency response approaches 20000, simulating strong CDC behavior, which, however, arises only from the contacts.

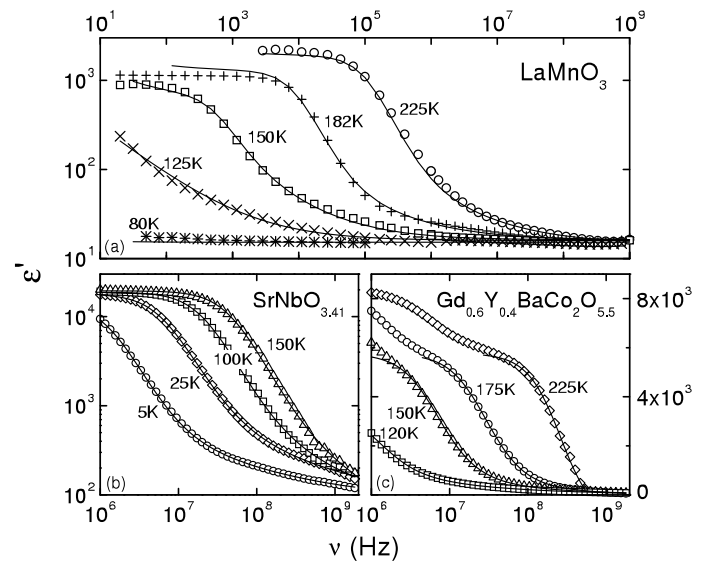


FIG. 3. Frequency-dependent dielectric constant of three transition-metal oxides for various temperatures. The lines are fits with the equivalent circuit shown in Fig. 1a. (a) Single-crystalline La_2MnO_3 [15]. (b) Single-crystalline $\text{SrNbO}_{3.41}$ [18]. (c) Polycrystalline $\text{Gd}_{0.6}\text{Y}_{0.4}\text{BaCo}_2\text{O}_{5.5}$ [19]. Here the fits were restricted to the high-frequency step, attributed to grain-boundary contributions [19].

Finally, in Fig. 3c we provide experimental evidence that in ceramic samples the response may be even more

complicated. Fig. 3c shows $\varepsilon'(\omega)$ for a perovskite-derived cobaltite [19] revealing clear evidence for two successive steps. The high-frequency step, yielding values of ε' close to 6000, is followed by a further increase towards low frequencies, which elevates ε' to 8000 at MHz frequencies and $T = 225$ K. While the low-frequency step is due to contact contributions, the second step can be attributed to grain boundary contributions, which yield a significantly different effective relaxation rate [19].

In conclusion, using a variety of different compounds we demonstrated the occurrence of apparent "colossal dielectric constants" at audio and radio frequencies over a broad temperature range. By an in-depth analysis of the frequency- and temperature-dependent dielectric response, all these CDCs were revealed to result from contact or grain boundary effects. In the case of CdF_2 : In we demonstrated how an extrinsic CDC can be excluded by investigating different contact configurations and different sample geometries. We strongly urge that in all further reports of CDC behavior, its intrinsic nature must be verified by a variation of contact type and/or sample geometry. Especially if the CDC exhibits a Debye-like relaxation process, an intrinsic source within the bulk sample is unlikely. In these cases it is advisable to analyze the data in terms of the equivalent circuits introduced decades ago [8,9], to obtain information on the true dielectric response of the sample material. This is also important for measurements on the divergence of the zero-temperature dielectric susceptibility in the insulating regime, which is one of the most important probes of a metal-to-insulator transition. To check this behavior experimentally [20] it seems important to correct the effective dielectric constants for contact contributions even at high temperatures.

Here it is also interesting to discuss the early results on charge-density wave (CDW) systems, which show CDCs at audio- and radiowave frequencies (see, e.g., [21]). One is tempted to assume that this behavior also results from the existence of depletion layers as outlined in this report. However, a detailed analysis of the dielectric response of $\text{K}_{0.3}\text{MoO}_3$, measured with different types of contacts, was performed by Cava *et al.* [21], excluding significant contact contributions. Furthermore, the unusually large low-frequency response of CDW systems has been explained theoretically by Littlewood to stem from pinned phason excitations [22].

In the materials investigated in the present work, the highest intrinsic dielectric constant observed is $\varepsilon' \approx 100$. What are the highest values of dielectric constants one can expect in bulk condensed matter systems? If the origin of the CDCs lies in colossal ionic or relaxational polarizabilities, they only can be reached in narrow temperature ranges close to ferroelectric (or relaxor ferroelectric) transitions, or over broader temperature ranges in incipient ferroelectrics, like in SrTiO_3 at low temperatures (see, e.g., [23]). If the CDCs result from electronic degrees of freedom in semiconductors, within a nearly free-electron model with an average energy gap E_g , high

values of ε' imply very low values of E_g [24]. In this case the dc conductivity certainly would dominate the dielectric response even at moderately elevated temperatures. Thus, with the exception of CDW systems, we believe that the uppermost limit of an intrinsic dielectric constant that can occur over broad temperature and frequency ranges will be of the order of $\varepsilon' \approx 10^2$.

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